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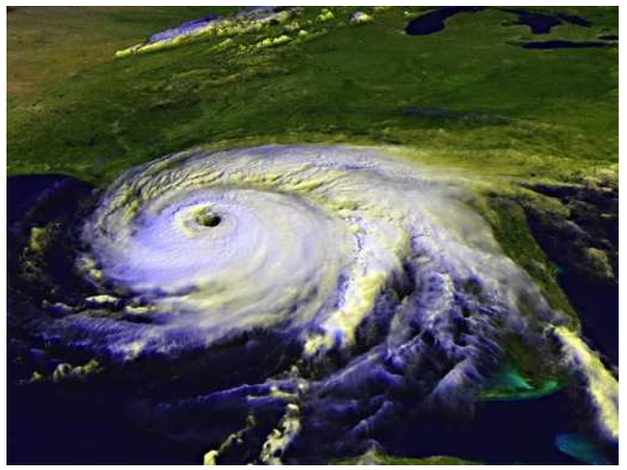

# Advanced Materials for Multi-Electron Redox Flow Batteries

Monday, September 26, 2016

Harry Pratt, Cy Fujimoto, Leo Small, Travis Anderson

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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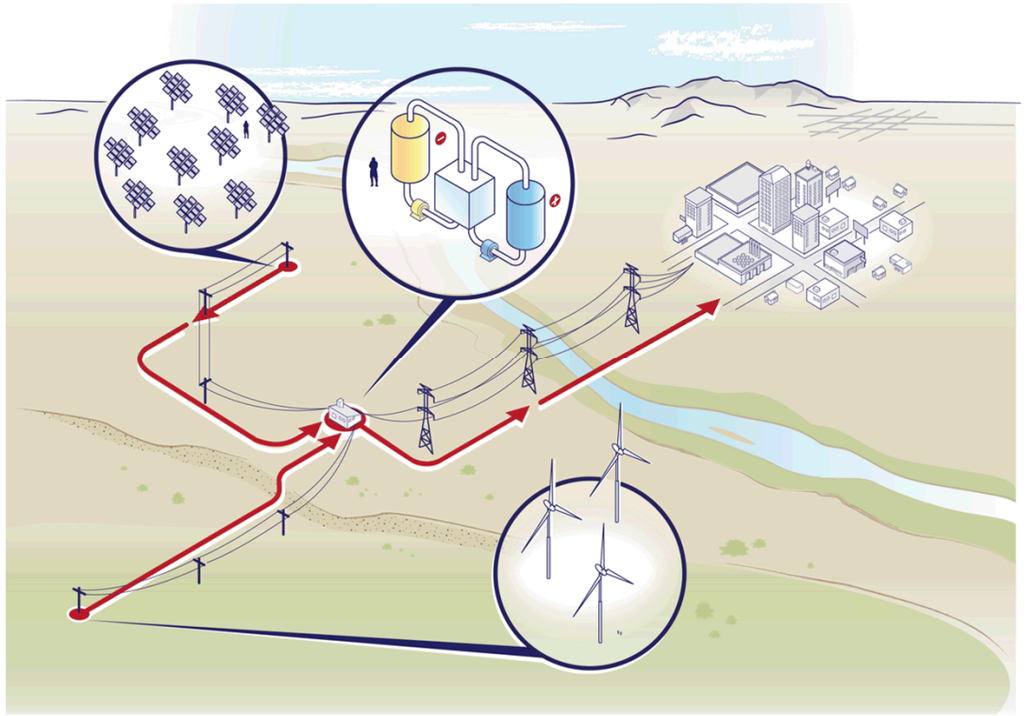
# Project Overview

**Problem:** Cost competitive ionic liquids have high viscosities but are promising for higher energy density redox flow batteries due to higher metal concentrations and wider voltage windows.

**Approach:** Couple earth-abundant electrolytes with commercial and custom membranes and rapidly test and tune in an iterative fashion using laboratory-scale cell designs.



**Increased renewables penetration on the grid**

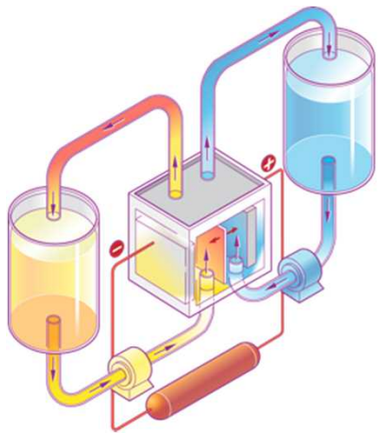
$$\textbf{Energy Density}_{RFB} \approx \tfrac{1}{2}nFV_{cell}c_{active}$$

$$ED_{AQ} = \tfrac{1}{2}1F1.5_{cell}2_{active} = \mathbf{1.5F}$$

$$ED_{IL} = \tfrac{1}{2}2F2_{cell}3_{active} = \mathbf{6.0F}$$

Potential for **four-fold** improvement

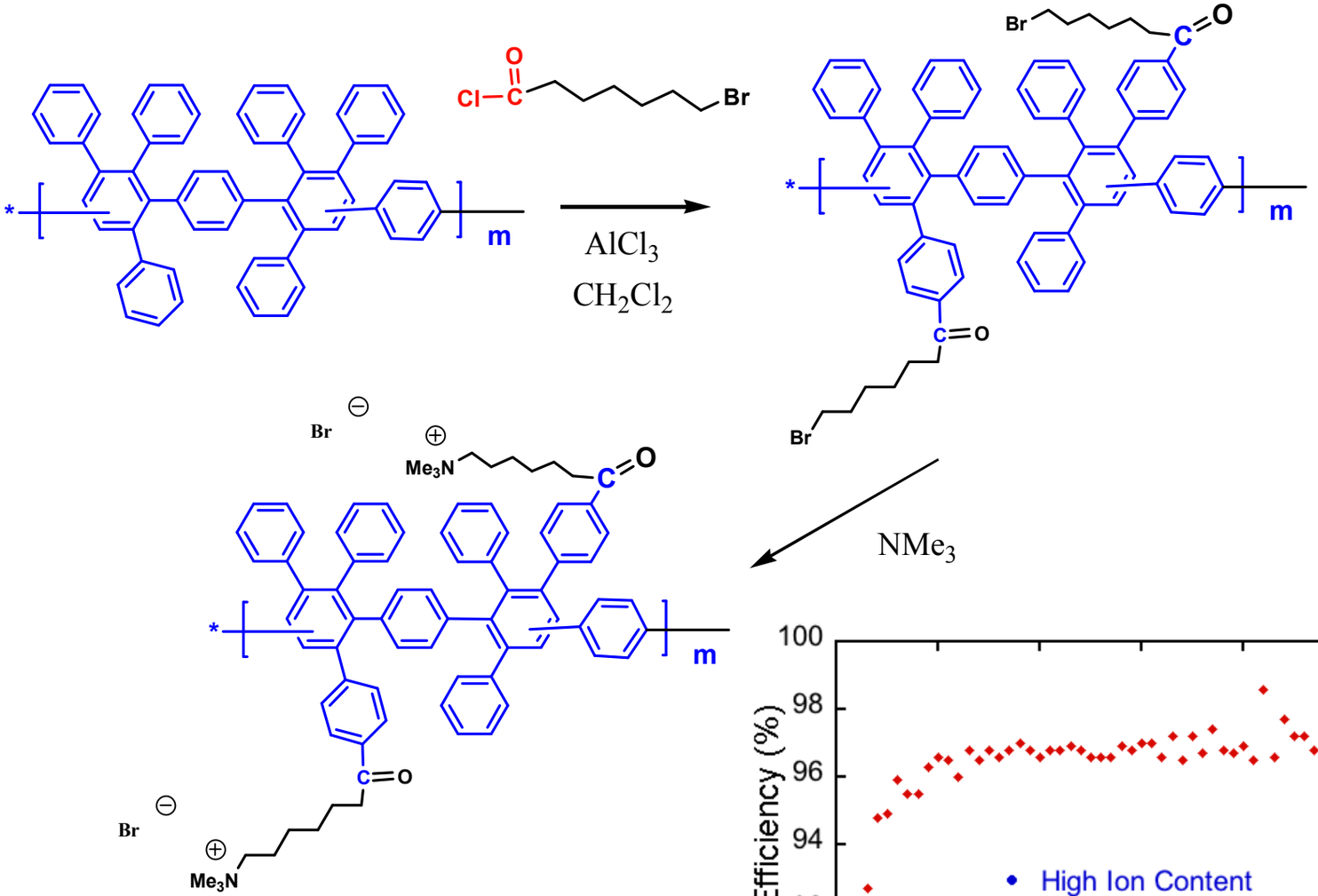
**MetIL$^-$**

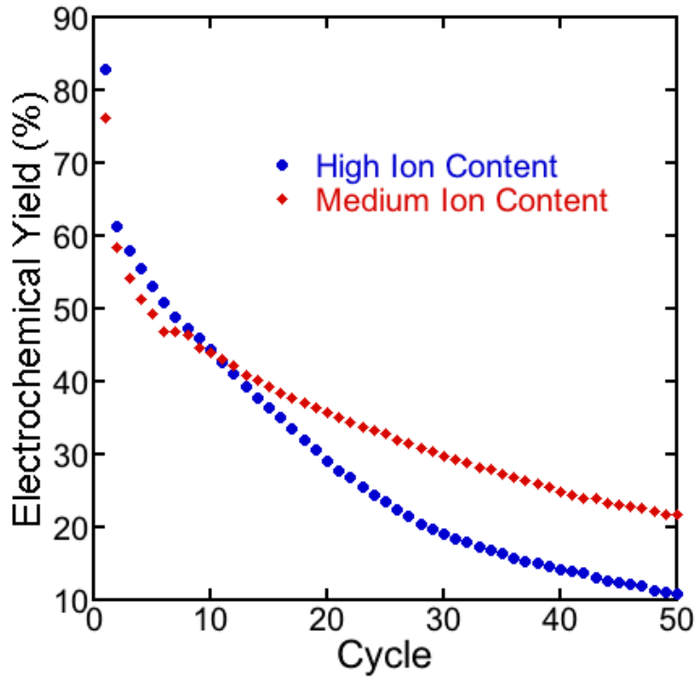


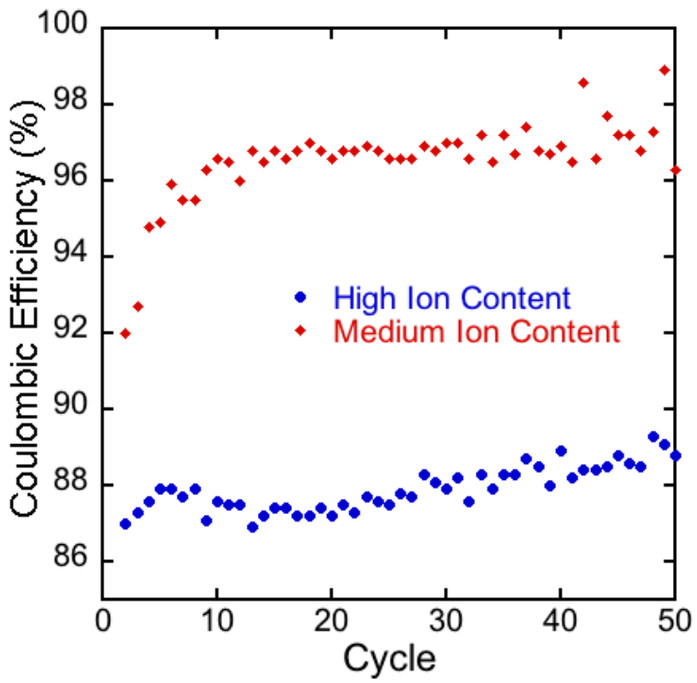
**$^+$MetIL**

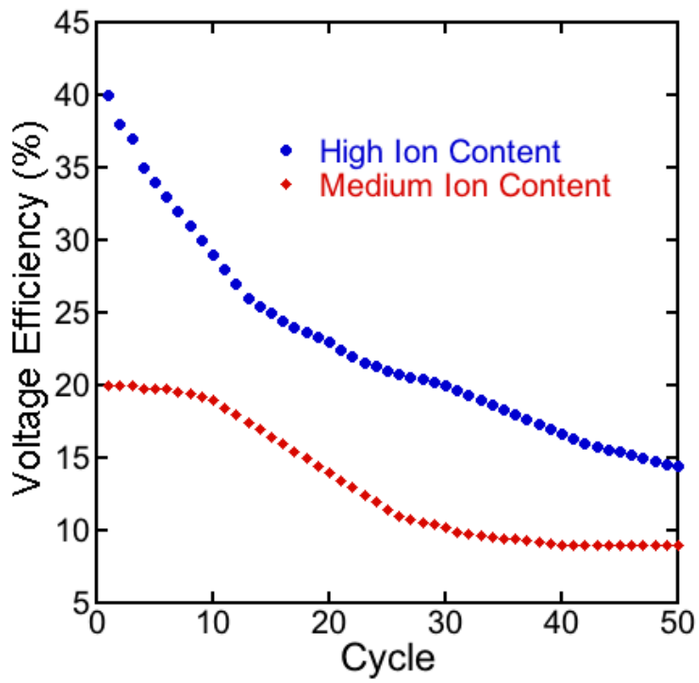
# Membrane Ion Content

## Membranes contain a polyphenylene backbone with pendant ionic groups; ionic content was varied qualitatively high, medium, and low.



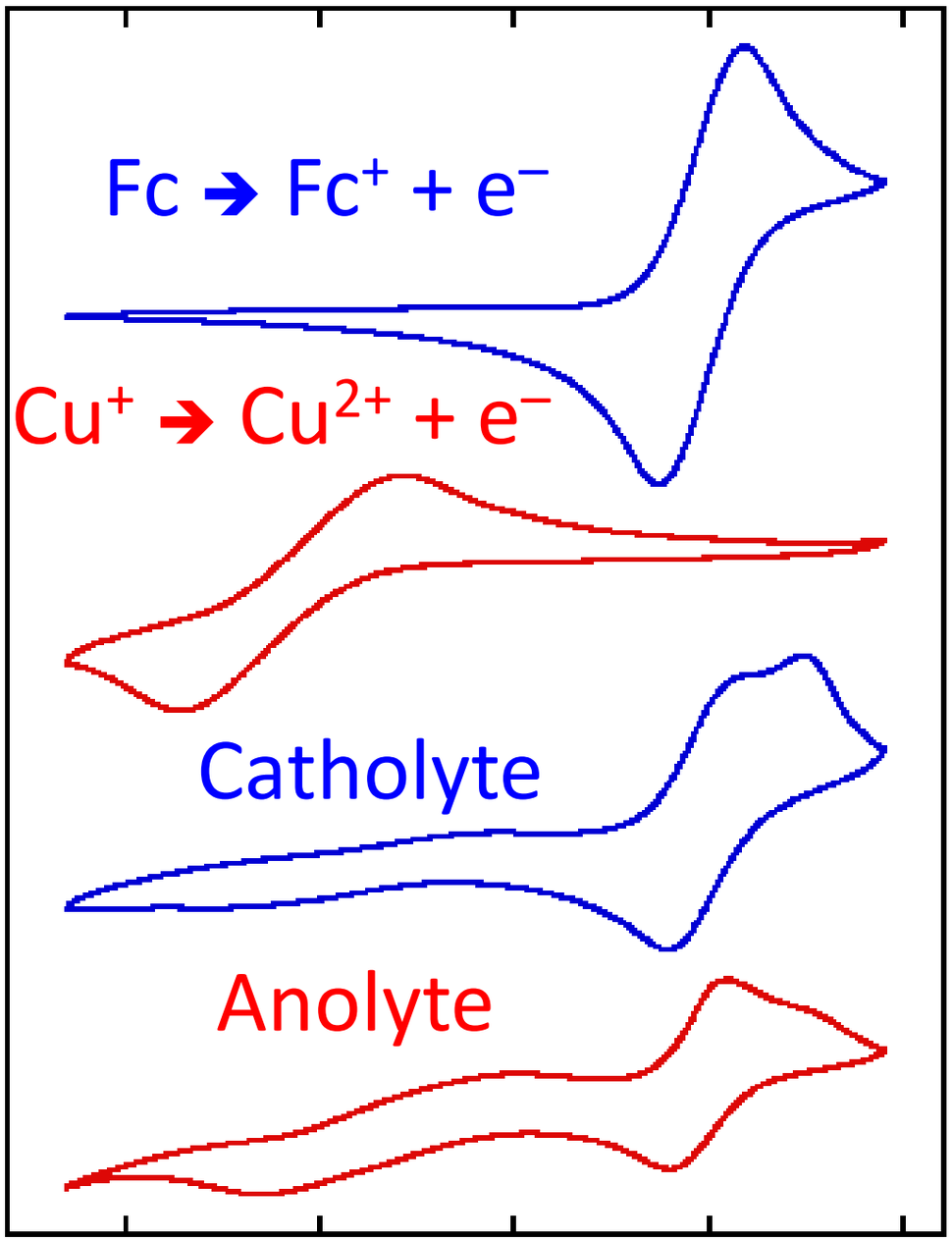



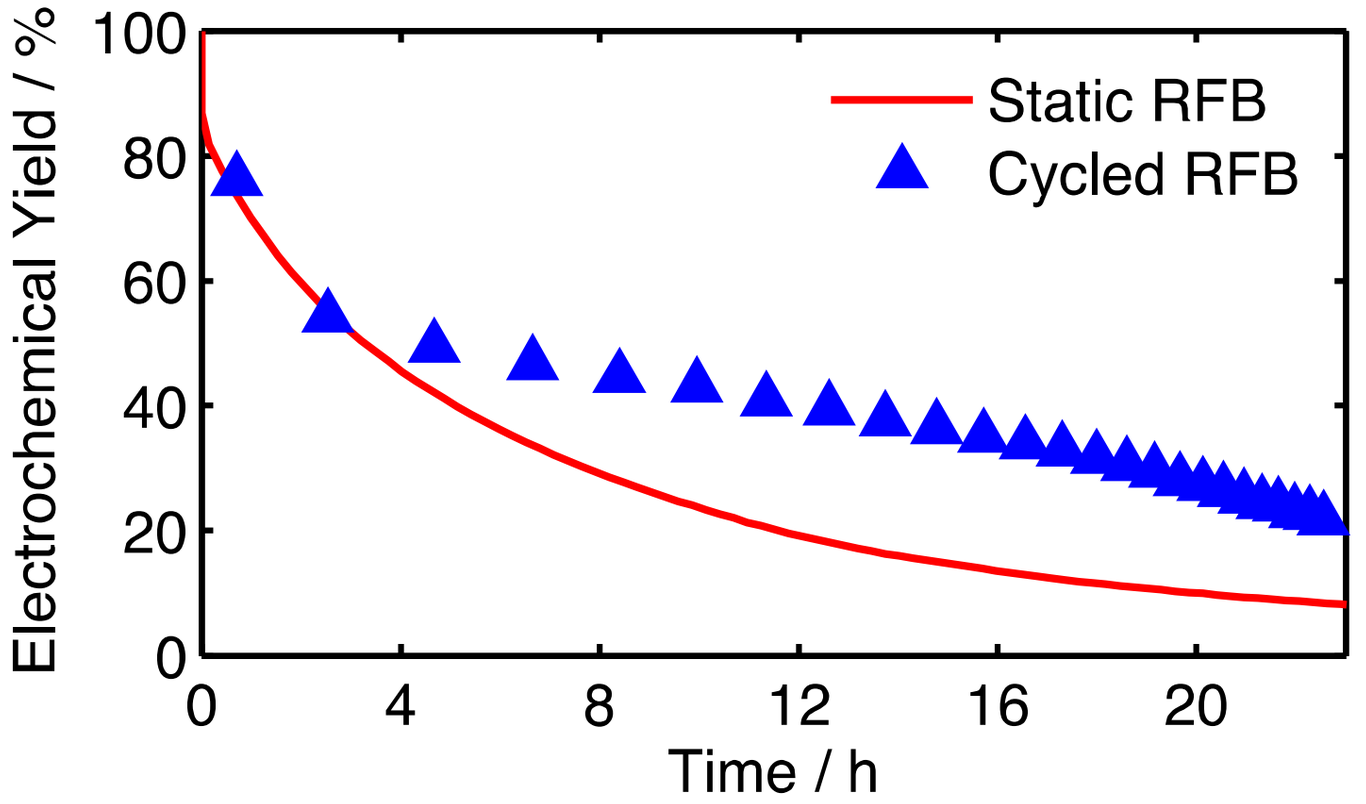






Small, Pratt, Fujimoto, and Anderson, *J. Electrochem. Soc.*, **2016**, A5106.

# Post Cycling Studies



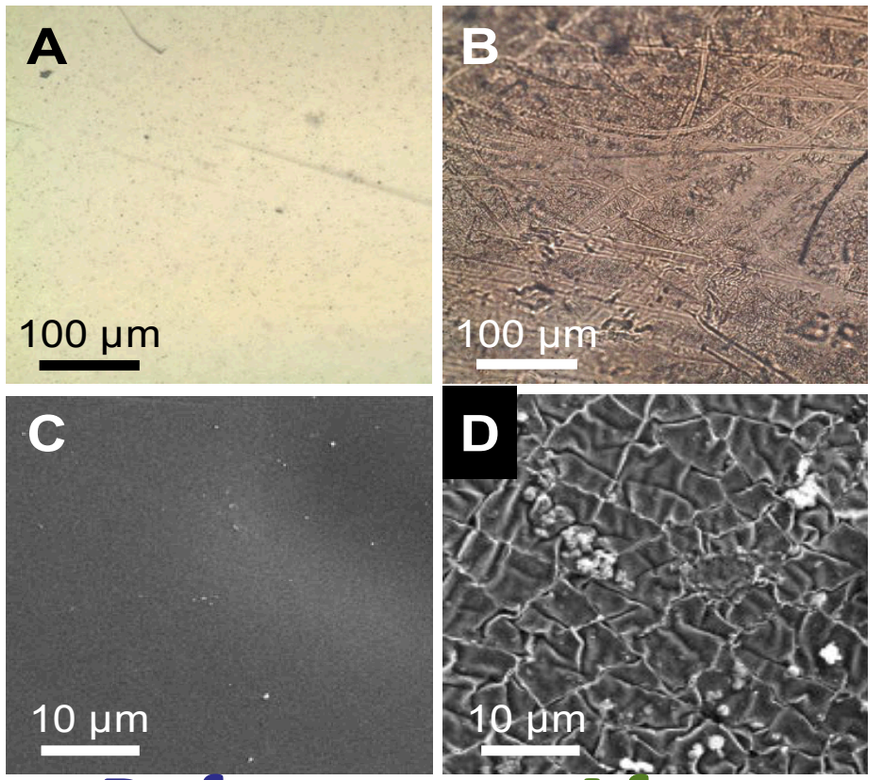




- The decreased electrochemical yield was investigated by (1) cycling rate effects; (2) crossover measurements; (3) impedance; (4) membrane stability.
- The CV as well as the overlay of the static and cycled data show that crossover was responsible for the lowered yield.



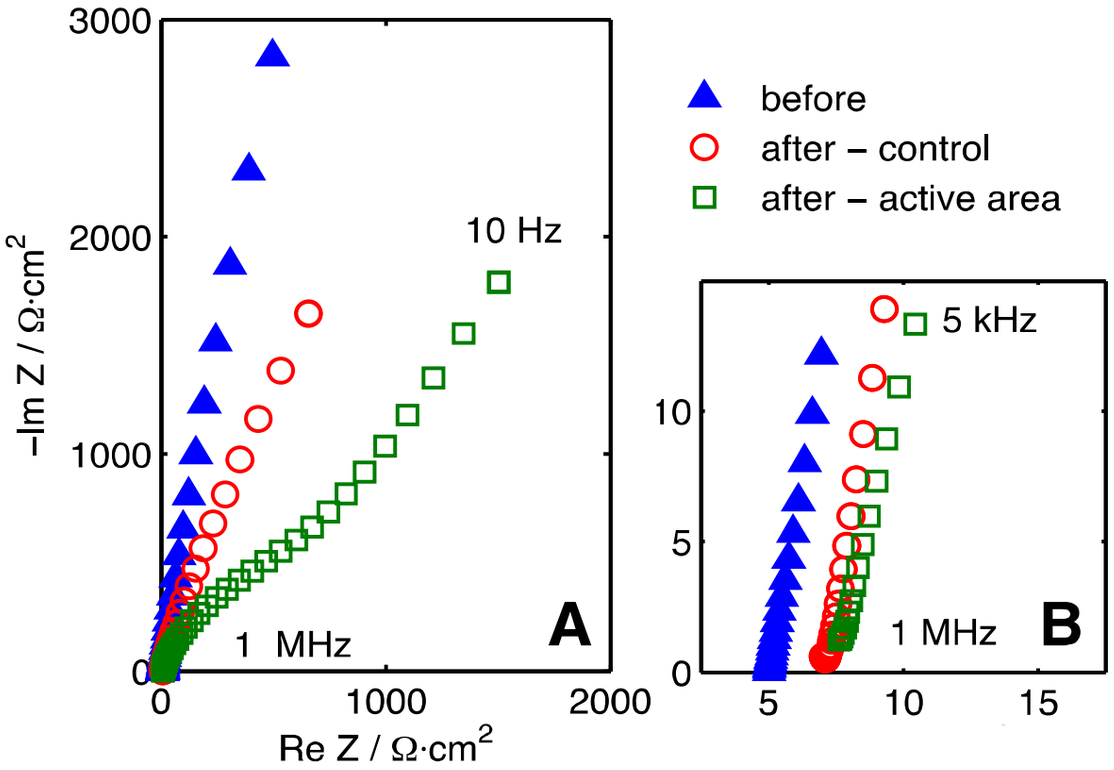
Small, Pratt, Fujimoto, and Anderson, *J. Electrochem. Soc.*, **2016**, A5106.

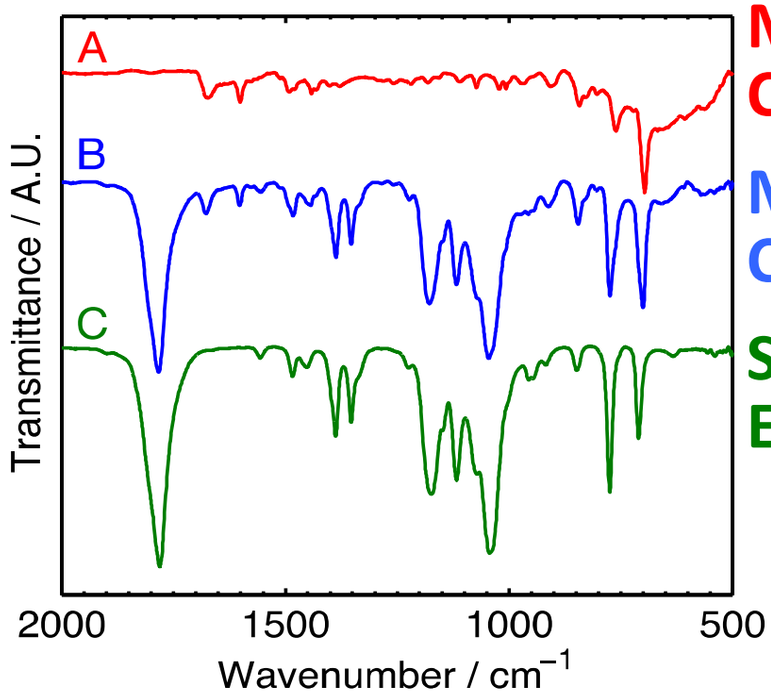
# Chemical Stability




**Before Cycling** **After Cycling**

- SEM and EDS data suggest that there was some decomposition of the ionic liquid.
- The increased resistance after cycling is attributed to the formation of a film on the surface of the membrane.




**Membrane Before Cycling**

**Membrane After Cycling**

**Supporting Electrolyte**

**Infrared data shows membrane is stable.**

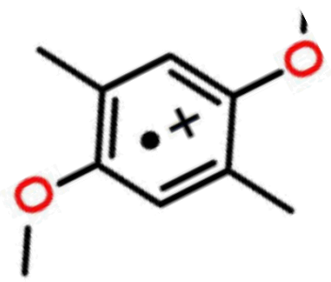


Small, Pratt, Fujimoto, and Anderson, *J. Electrochem. Soc.*, **2016**, A5106.

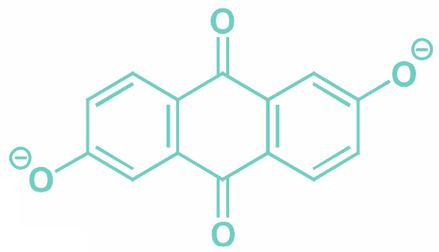
# Increasing Energy Density

## Recently a number of groundbreaking solutions to higher energy density have appeared.

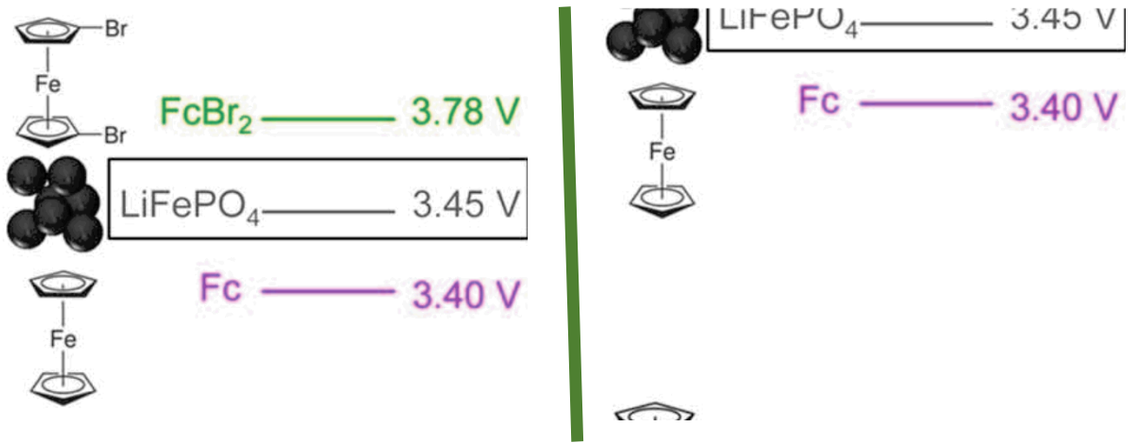
"Lightest Organic Radical Cation…"
Huang, Wang, et. al, *Science Reports,* 2016



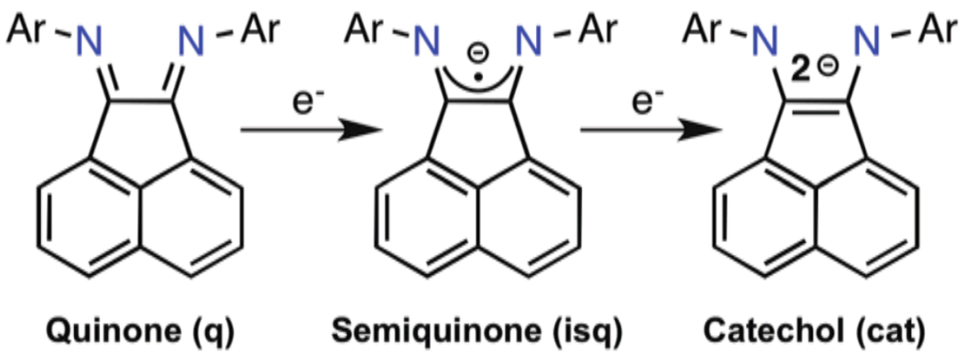
"Alkaline Quinone Flow Battery"
Lin, Aziz, et. al, *Science,* 2016




"High-energy density non-aqueous …"
Jia et. al, *Science Adv.,* 2016




"Voltage Clustering in Redox-Active Ligands…"
Zarkesh, Anstey, et. al, *Dalton Trans.,* 2016




**Can we make the solvent and supporting electrolyte "filler" electrochemically active?**

# Increasing Energy Density–Strategy

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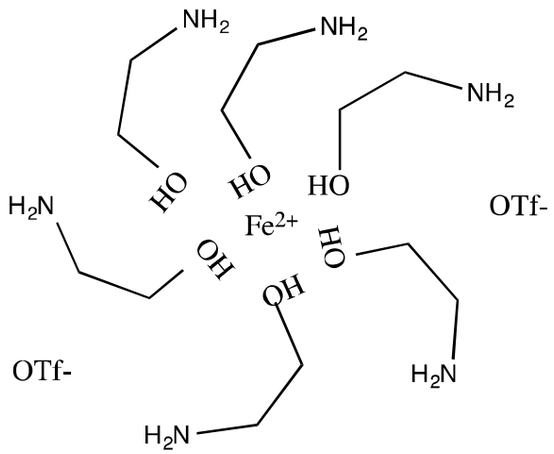
**Start with Sandia's MetILs and replace increasing amounts of "filler" with redox active compounds ($I^-$, Fc) until it becomes impractical.**




Couple FcCOOH to 1st ligand

$T_{melt}$ ~70 °C

Couple FcCOOH to 2nd ligand

$T_{melt}$ >100 °C

Replace 1st $OTf^-$ with redox-active $I^-$

Single liquid phase at 25 °C

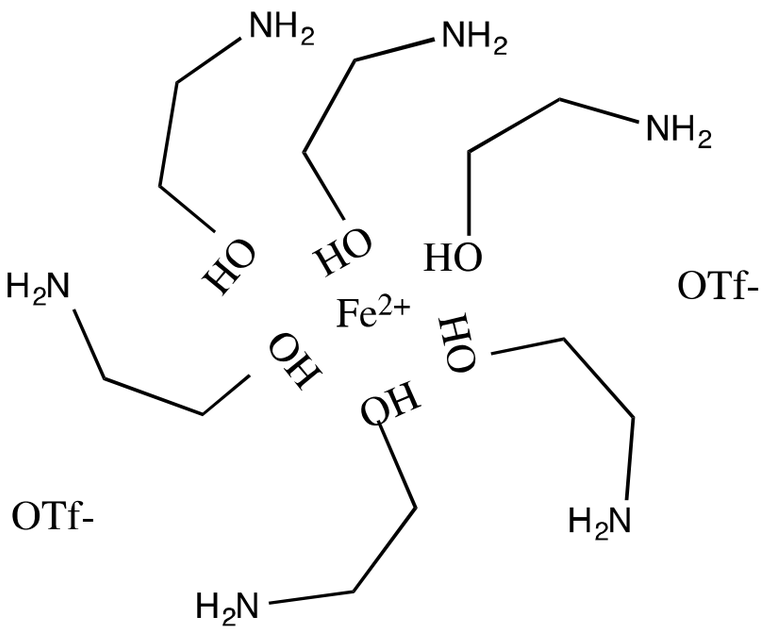
$T_{melt}$ ~60 °C Single liquid phase

Replace 2nd $OTf^-$ with redox-active $I^-$

Phase separation

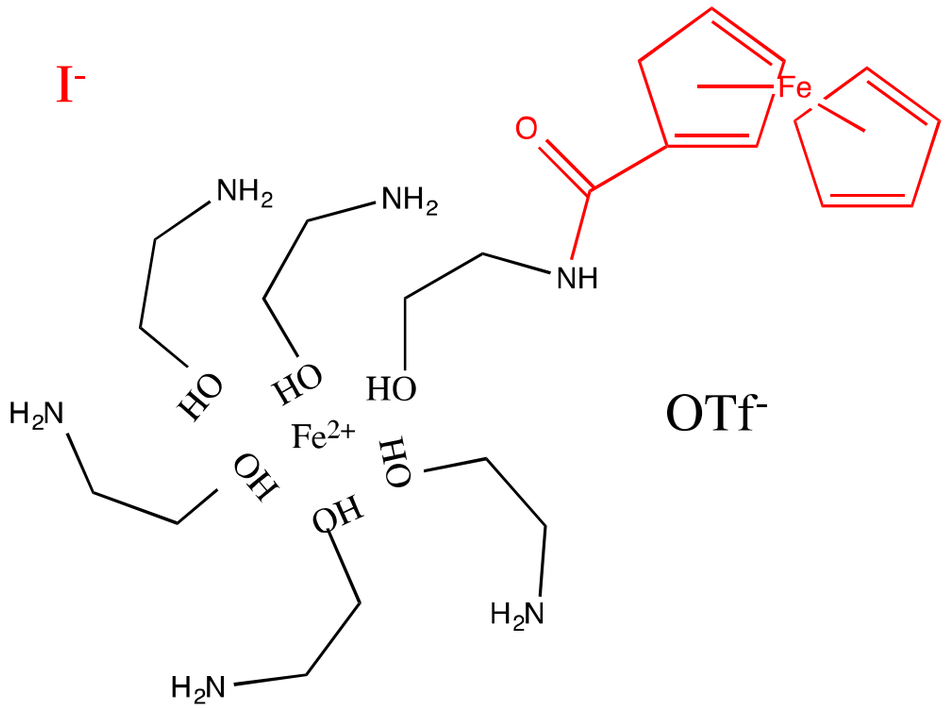
# MetILs[3]

## Fe-MetIL




**Redox activity added to the ligands and anions**

## Fe-MetIL[3]




**2.8 M redox-active $e^-$**

$Fe^{2+} \rightarrow Fe^{3+} + e^-$

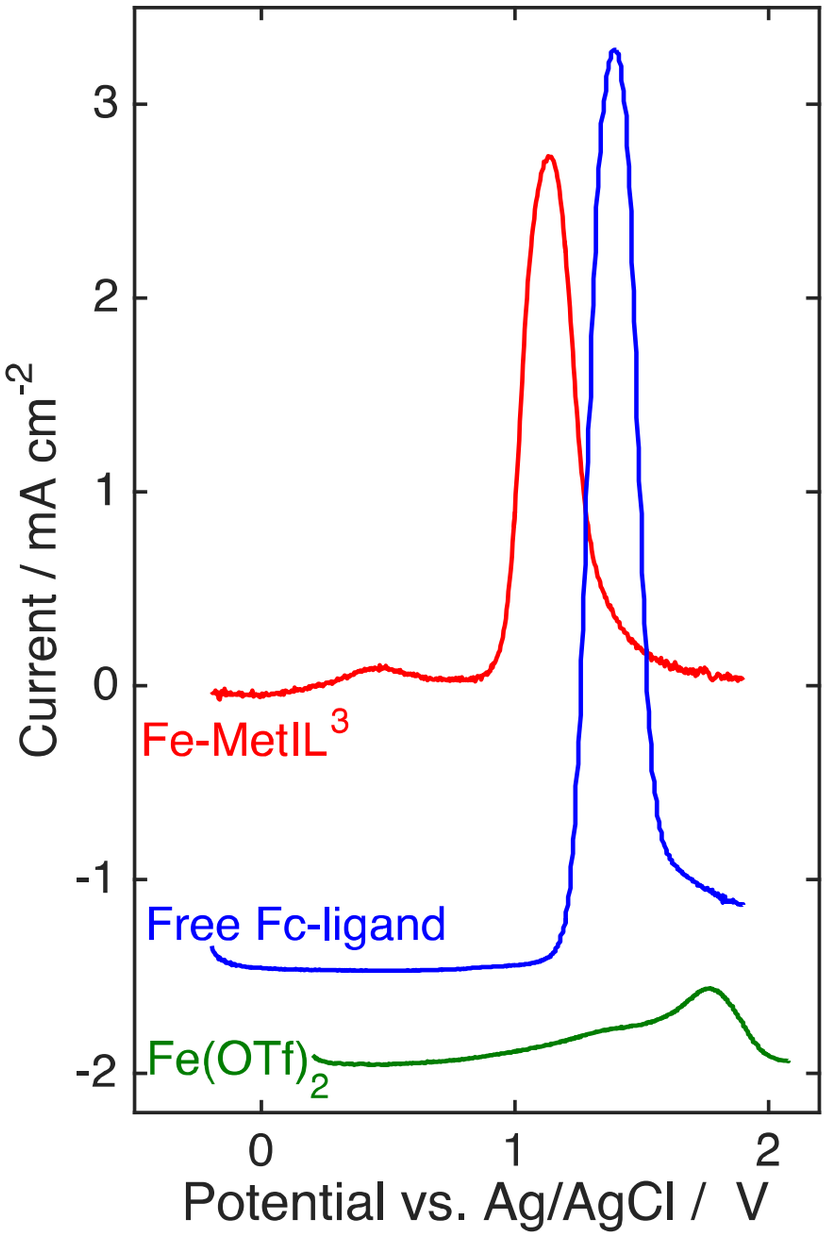
**7.4 M redox-active $e^-$**

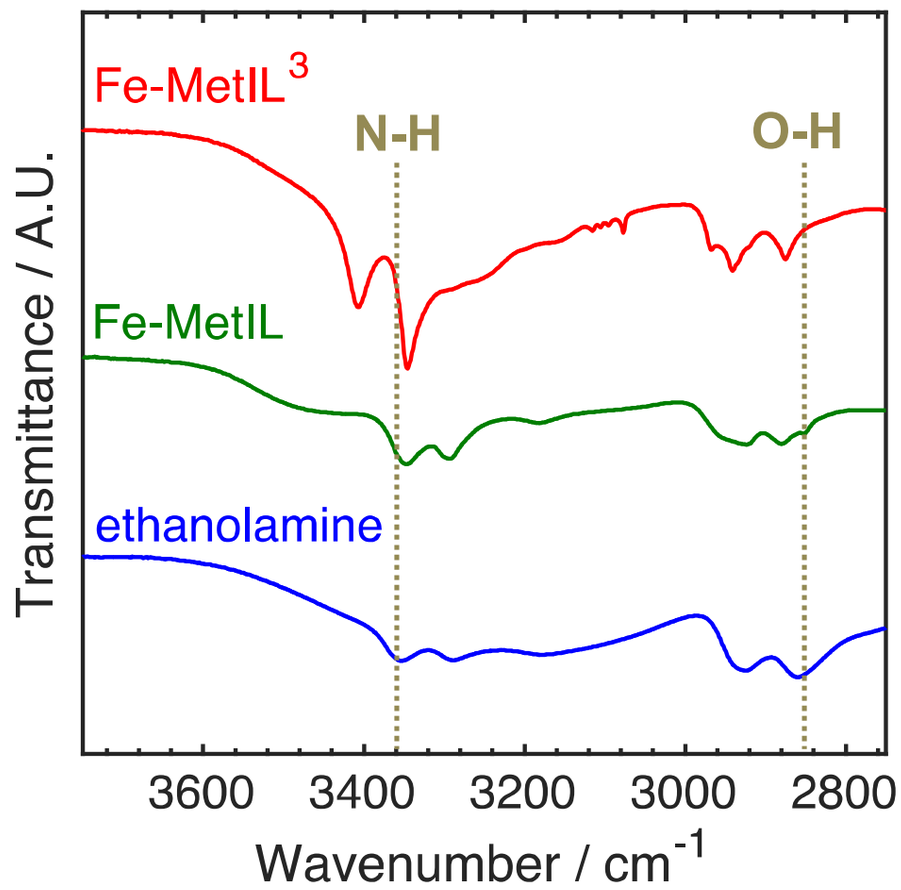
$Fe^{2+} \rightarrow Fe^{3+} + e^-$

$Fc \rightarrow Fc^+ + e^-$

$3I^- \rightarrow I_3^- + 2e^-$

# MetILs[3] Characterization




| 54 (N-H) | 2860 (O-H) |
|---|---|
| 7 | 20 |
| 8 | 15 |

**$Fe^{2+}$ and Fc-ligand shift to lower potentials when MetIL forms**

**Ethanolamine O-H and N-H IR peaks shift upon complexation**

# MetILs[3] Initial Flow Cell Studies

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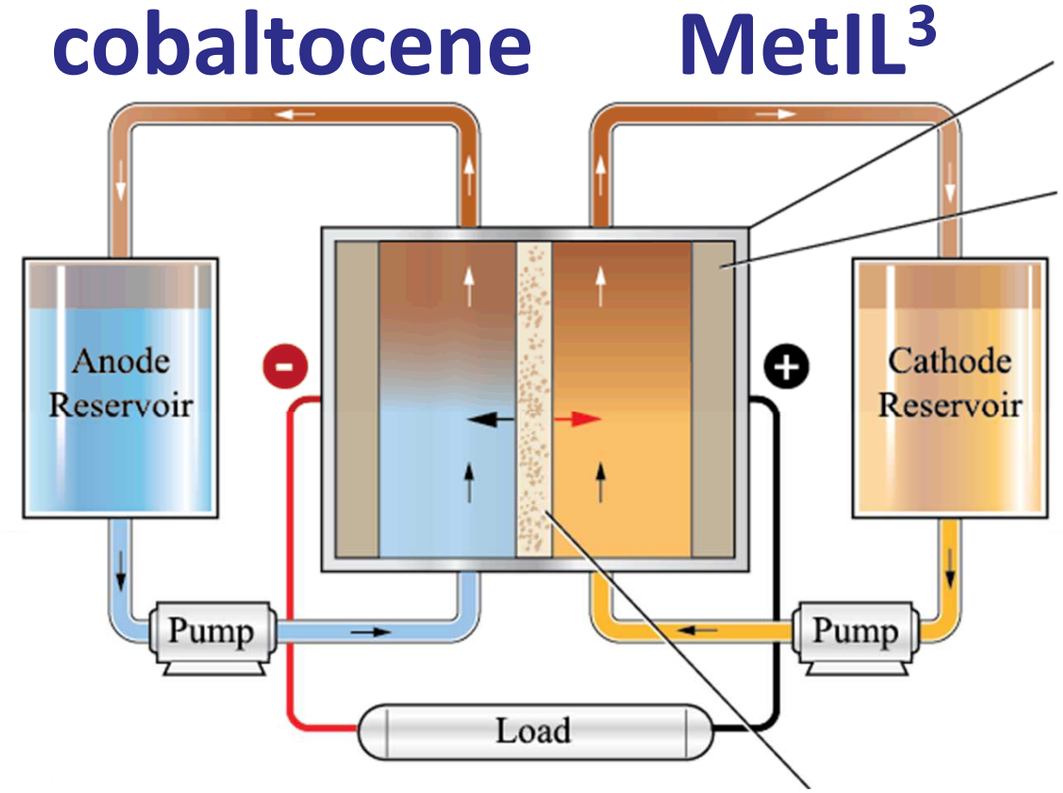
**cobaltocene** **MetIL[3]**

$Cc \rightarrow Cc^+ + e^-$

200 mM
0.5 M $LiNTf_2$ in PC
5 mA/cm²




$Fe^{3+} + e^- \rightarrow Fe^{3+}$

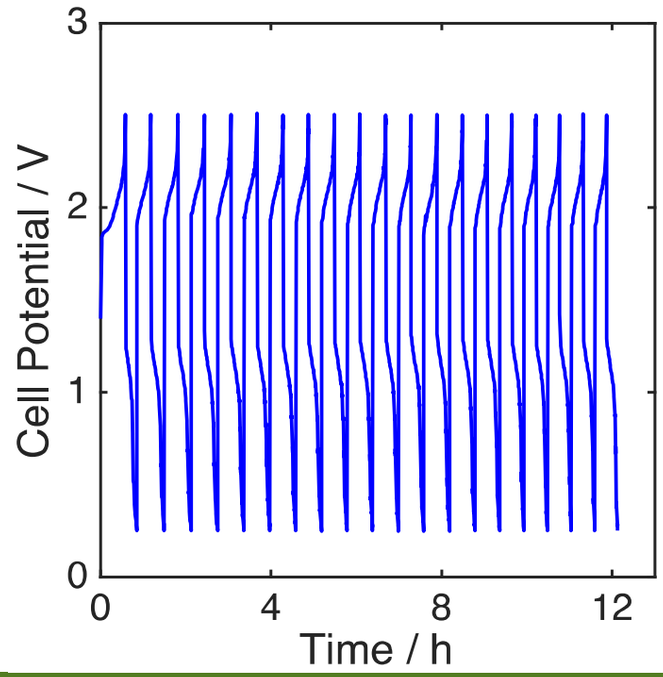
$Fc^+ + e^- \rightarrow Fc$

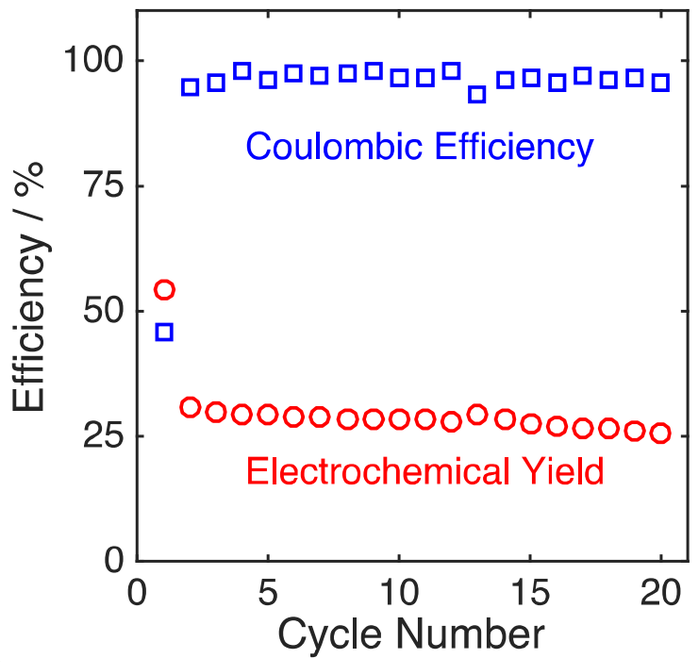
$I_3^- + 2e^- \rightarrow 3I^-$

100 mM
0.5 M $LiNTf_2$ in PC
5 mA/cm²

**Membrane: Fumasep FAP-PK (anion exchange)**

**Cell shows good cyclability after initial capacity loss.**



# Mediated Flow Batteries

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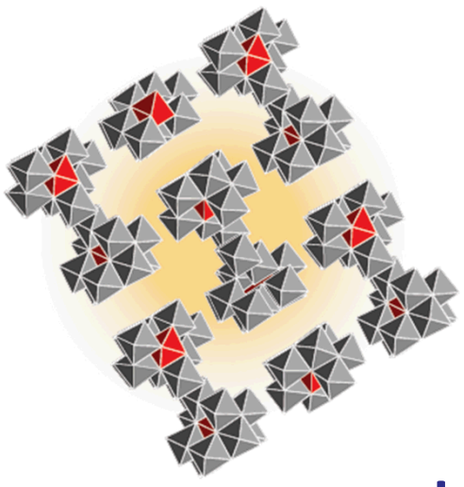
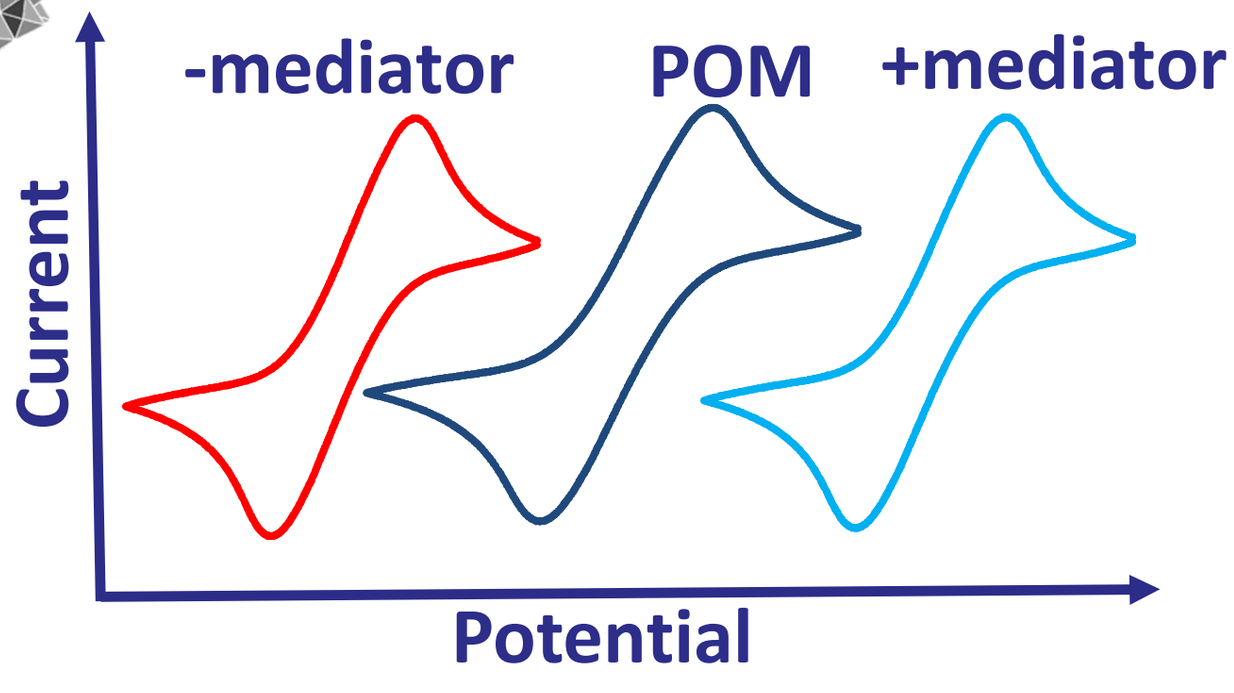
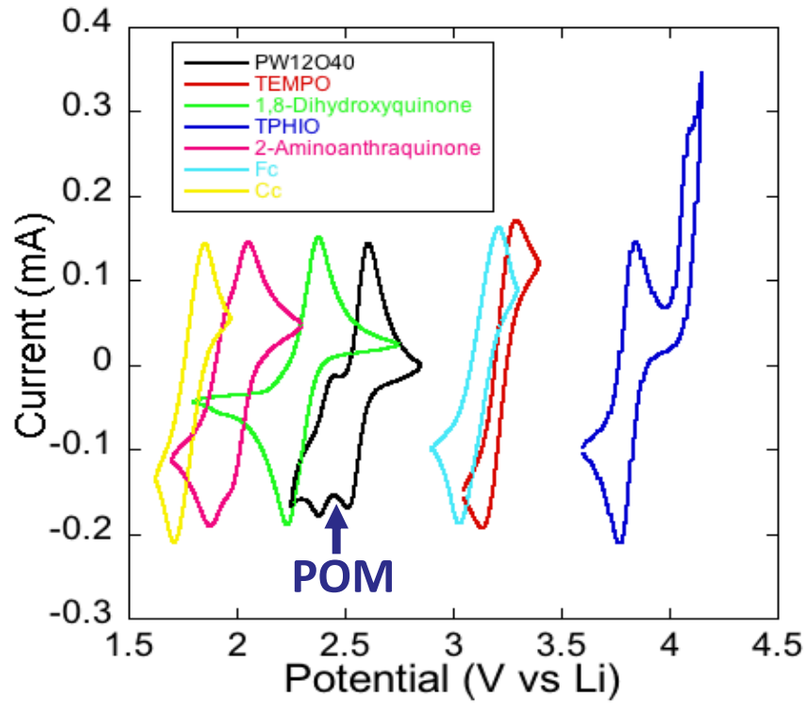
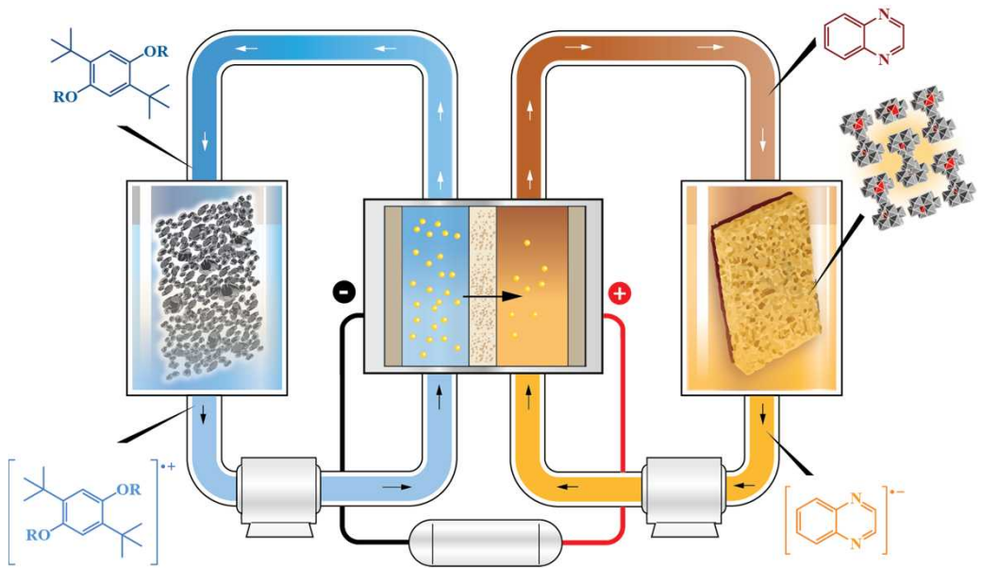


## Polyoxometalate (POM) cathode: $Na_3PW_{12}O_{40}$

$$PW_{12}O_{40}^{3-} + 24e^- \rightarrow PW_{12}O_{40}^{27-}$$




- energy stored in easily exchangeable canisters of material
- mediators serve as redox shuttles between electrodes and canisters
- polyoxometalates may be substituted with traditional lithium intercalation materials

# Summary and Acknowledgements

- Diels Alder polyphenylene membranes with tunable ion content provide an alternative to commercial systems.
- MetILs$^3$ utilizes electrolyte “filler” to increase theoretical energy density 3X from 190 to 620 Wh/L over MetILs.
- In 2016 the team published two new papers including one featured on the cover of *Journal of Materials Chemistry A* and was granted one new patent.

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